

BAKERIAN LECTURE.—“On the Constitution of the Copper-Tin Series of Alloys.” By C. T. HEYCOCK, F.R.S., and F. H. NEVILLE, F.R.S. Received February 26,—Lecture delivered February 26, 1903.

(Abstract.)

This paper is an attempt to fill a very serious gap in the study of alloys. As a rule, an alloy begins to be interesting when the temperature of the liquid alloy has fallen to its freezing point. This point, which records the moment when solid first appears in the liquid, is easily observed on account of the evolution of latent heat that occurs on the formation of solid, and if the freezing points of all the alloys of a series are determined, we can plot the freezing-point curve. Many such curves have been traced in the last ten years: that of the copper-tin alloys is given by the upper line in our diagram. The curve consists of several branches cutting each other in angular points. The one thing that these curves record without ambiguity is the number of different solids that can crystallise out of the liquid alloys, for each branch corresponds to the crystallisation of a different substance. But this is almost all that such curves tell us with certainty. They do not tell us whether the solids forming are the pure metals, or pure compounds, or crystalline solid solutions of the metals. Other experiments are needed to decide such questions.

The other great branch of the study of alloys consists in the microscopic examination of the solid alloys after they have cooled to ordinary temperature, that is to say, after they have, in general, ceased to undergo change. Between these two series of experiments there is an enormous gap of temperature, it may be 1000 or 500 degrees, and it is in this range of temperature that the whole life-history of the alloy, regarded as an organism, is to be found. The only fruitful experiments we know of dealing with this intermediate region are the cooling curves of Roberts-Austen and Stansfield. These observers traced automatically the whole of the cooling of the bronzes and obtained some remarkable results. They found that the evolution of heat at the freezing point was often succeeded at much lower temperatures by other evolutions of heat, and that many of these must have occurred after the alloy had wholly solidified. These thermal changes point to important chemical or physical changes, though they do not tell us what these changes are. They suggest, however, that the final patterns found by the microscope in the solid alloys are likely to be very complicated, as they may contain several records superposed the one on the other. We found these patterns very beautiful, but hopelessly complicated.

It occurred to us, and this is the method of the paper, that we could simplify the phenomena by a systematic chilling of the ingots at selected temperatures. A number of small ingots of the same alloy were placed in separate tubes in a bath of tin, together with a recording pyrometer, the temperature was raised above the freezing point of the alloy, and the whole very slowly cooled, the slow cooling being an essential feature of the experiment. Ingots were then extracted at selected temperatures and rapidly chilled by immersion in water. The microscopic examination of these chilled ingots showed that it was quite easy to distinguish the large crystals, that had formed during the slow cooling preceding the chill, from the matter that was liquid when the ingot was withdrawn from the furnace.

Successive chills of an alloy exhibit the solid growing in amount as the temperature falls, and finally show the ingot completely full of solid. We thus obtain, with very reasonable accuracy, the temperature of complete solidification of the alloy; and by applying the method to alloys with different percentages of tin we have traced a new curve, the "solidus," or curve of complete solidification. The solidus of the bronzes is the second line of the diagram. It is a remarkable line, made up of sloping, horizontal and vertical branches. As in the freezing-point curve, each branch corresponds to the crystallisation of a different solid.

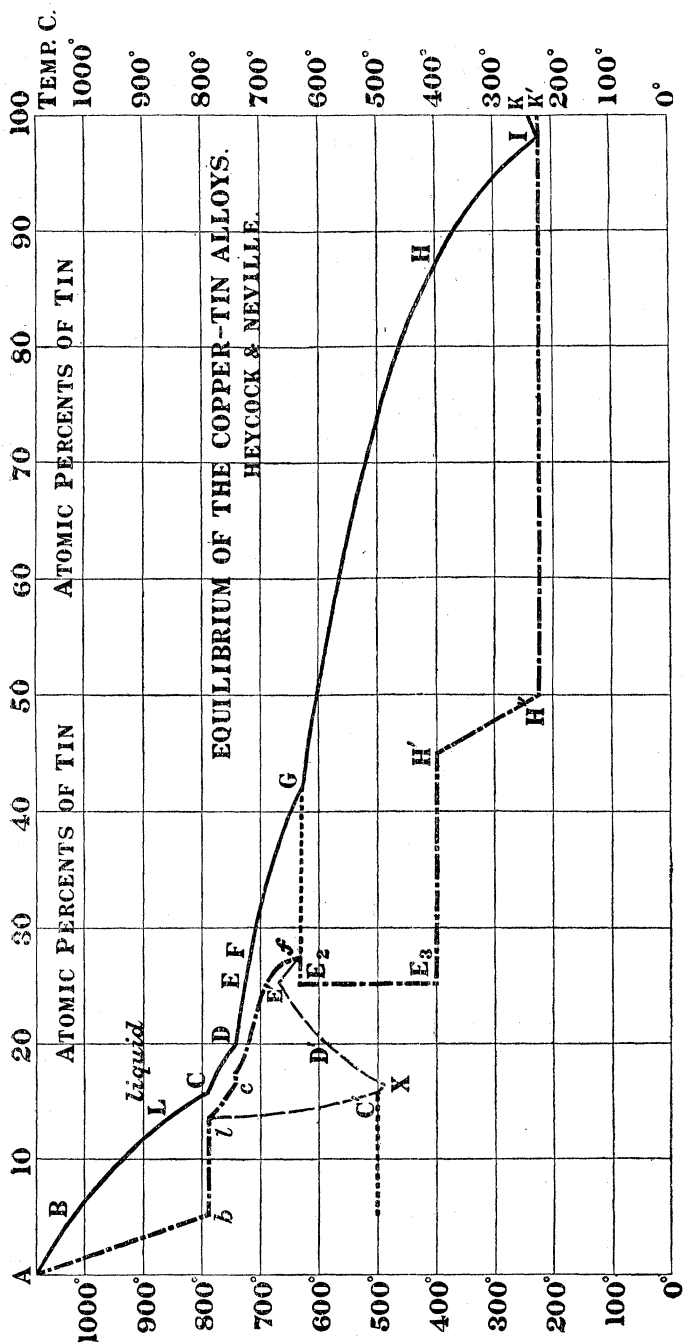
In the notation of Professor Roozeboom, the upper curve ABC...I, is called the liquidus, because all wholly liquid alloys lie above it; and the solidus, *AbledefE₂E₃H'H'I*, is so named because all wholly solid alloys lie below it.

The solidus of the bronzes is remarkable for the very narrow range of temperature within which some alloys pass from the wholly liquid to the wholly solid state.

According to Roozeboom's theory, each sloping branch of the solidus, and there are four such in the diagram, corresponds to the crystallisation out of the liquid of a different series of solid solutions, each vertical part to the crystallisation of a pure body, and each horizontal part to the case of the solid alloy at temperatures immediately below the solidus, being a complex of two substances. Our examination of the chilled ingots has completely verified all these statements.

The evolutions of heat observed by Roberts-Austen and Stansfield at temperatures corresponding to the point C, D, G and H are due to definite chemical transformations in which one solid is decomposed and another is formed. Chills taken immediately above and below these critical temperatures reveal the nature of each change most clearly.

The transformations at C, D, and especially at H, are very slow and do not become complete unless the temperature is maintained constant for hours or days at a point slightly below the transformation temperature, but all these changes can be made to agree exactly with



theory if time is allowed for them. The change at the G temperature is the breaking up of a solid solution into a mixture of the compound Cu_3Sn and liquid, and is instantaneous: here we have a case of a solid partially melting as it cools.

The curve $\text{IXE}'f$ forms with the part of the solidus immediately above it an area, roughly triangular, within which all the alloys appear to be uniform solid solutions, but, as soon as an alloy cools to the curve, it becomes saturated and a new body crystallises out of the solid solution. One branch of the curve $\text{IXE}'f$ corresponds to the crystallisation of a body rich in copper, the other to the crystallisation of a body rich in tin, which is probably the pure compound Cu_4Sn . The angle X (or rather C'), is the eutectic angle at which both bodies crystallise together, the whole phenomenon being exactly like crystallisation out of a liquid.

All the results obtained from the study of the chilled alloys are in harmony with the pyrometric work of Roberts-Austen and Stansfield, and many of the changes we have examined correspond to an evolution of heat recorded by them.

The paper is an extension of a short paper published by us in the 'Proceedings' of December, 1901.

"On the Formation of Barrier Reefs and of the Different Types of Atolls." By ALEXANDER AGASSIZ, For. Mem. R.S. Received February 7,—Read March 19, 1903.

The results here presented are based upon observations carried on during the past 25 years in Florida, the Bermudas, Bahamas, Cuba, Jamaica, and the West Indies in the Atlantic. They include in the Pacific the Galapagos, the Hawaiian Islands, the Great Barrier Reef of Australia, the Fiji Islands, and the Coral Reefs and Islands of the tropical Pacific, from the Marquesas to the Paumotus, the Society Islands, the Cook Archipelago, Niue, the Tonga, Ellice, Gilbert, and Marshall Islands, the Carolines and Southern Ladrões, and the Maldives, in the Indian Ocean.

Recognising that Darwin's theory did not explain the conditions observed, my reports were limited to descriptions of the different types of Coral reefs and of the causes to which they probably owed their formation, and no attempt was made to establish any independent general theory.

Beginning with the Barrier Reefs, we find that those of Fiji, the Hawaiian Islands, and the West Indies usually flank volcanic islands and are underlaid by volcanic rocks. Those of New Caledonia,